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Copper β -trinitrocorrolates

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Abstract

The β -nitration reaction carried out on the corrole macrocycle has been shown to be extremely regioselective, although the reduced symmetry of the macrocycle could potentially lead to a huge number of possible regioisomers. We recently reported that the careful use of $\text{AgNO}_2/\text{NaNO}_2$ as a nitrating system enabled the achievement in good yields of mono- and dinitro-derivatives on both corrole free base and its copper complex, proving to be an efficient and cost-effective method. In this work, we present a detailed study of the scope of this method using TtBuCorrH_3 as a model corrole. A further increase of the oxidant pushes the nitration up to the functionalization of three β -pyrrolic positions, although concomitant decomposition of the macrocycle is also observed. The application of the proven nitration method with a five-fold excess of both silver and sodium nitrites with respect to corrole, afforded the $2,3,17\text{-(NO}_2)_3\text{-TtBuPCorrCu}$ as the main product, in 25% yield, together with traces of another compound identified by X-ray crystallographic analysis as the $3,8,17\text{-(NO}_2)_3\text{-TtBuPCorrCu}$ isomer. In light of these recent results, we also reinvestigated the characterization of the nitration products obtained from bis-substitution reactions, allowing among others the identification of the copper $3,8\text{-(NO}_2)_2$ corrolate.

Keywords

corrole; β -functionalization; nitration; AgNO_2

INTRODUCTION

The definition of corrole as “the little big porphyrinoid” [1a], summarizes in just a few words the peculiar properties of this macrocycle, for which the lack of one *meso* carbon bridge compared with porphyrins, has interesting repercussions on both coordination properties and chemical reactivity of the peripheral positions, which can be selectively transformed [1]. All these feasible manipulations of the corrole skeleton allowed exploitation of this macrocycle in different applications [2], such as for example the use of a Ga(III)-substituted amphiphilic corrole in anticancer therapy [3].

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¹H NMR spectra of the prepared compounds (Figs S1–S10) are given in the supplementary material. This material is available free of charge via the Internet at <http://www.worldscinet.com/jpp/jpp.shtml>.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-912670.

Copies can be obtained on request, free of charge, via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

The introduction of specific functionalities at the corrole periphery is particularly appealing since this action can alter some of the macrocycle properties. The derivatization of the β -positions of corroles with halogens [4] or boryl groups [5] can be exploited for the modification of the corrole moiety by Pd or Ir-catalyzed coupling reactions, while functionalization with charged groups such as carboxylate [6], sulfonate [7] or pyridinium [8], can enhance the solubility of corroles in aqueous media, allowing for their investigation in biological environments.

In the last few years, our efforts have been focused on the development of synthetic protocols for the introduction of one or more $-\text{NO}_2$ groups at the corrole β -pyrrolic positions [9], the main reason being related with the impressive chemical versatility of this functional group. Its transformation into the amino group, with all the subsequent possible organic reactions, or its direct involvement in activating aromatic nucleophilic substitution at close pyrrolic carbon atoms, are some of the potential uses of nitrocorroles that are under study in our laboratories. For example, we recently reported the synthesis of β -amino- β -nitrocorrole derivatives through the nucleophilic attack of 4-amino-4*H*-1,2,4-triazole on copper and germanium- $-(\text{NO}_2)$ corrolates, demonstrating the susceptibility of the corrole macrocycle towards reactions with nucleophiles, regardless of its high electron-density [9b]. Possessing strong π -acceptor properties, the nitro group strongly interacts with the corrole- π -system, altering the spectroscopic and redox properties of the macrocycle, especially when the $-\text{NO}_2$ is located at the 2-position, where more efficient conjugation is allowed for steric reasons [9c].

All these aspects prompted us to study the nitration reaction in depth and, to date, we have provided several synthetic methodologies, applying various nitrating systems to achieve β -nitro-derivatives of Cu [9b], Ge [10], Ag [9a], Fe [11] and Co [12] corrolates. Very recently, we have reported the preparation of β -nitro-5,10,15-tritolyllcorroles [9c], which represents the first example of selective β -nitration on the corrole free base and potentially opens the way to novel complexes of β -nitrocorroles upon metal insertion. The reaction of TTCorrH_3 with the $\text{AgNO}_2/\text{NaNO}_2$ system afforded the mono- and di-nitrocorrole derivatives in satisfying yields when the nature of the oxidant was carefully chosen. Although the reaction was demonstrated to be regioselective, giving the 3- NO_2 and the 3,17- $(\text{NO}_2)_2$ isomers as the main reaction products, it was also possible to identify traces of other regioisomers formed during the reactions, namely the 2- NO_2 , 2,3- $(\text{NO}_2)_2$ and 3,12- $(\text{NO}_2)_2$ compounds. The detection of the latter isomer was particularly unexpected, because it represented the first example of bis-functionalization occurring on antipodal pyrroles A and C while leaving the C17 and C18 carbons unsubstituted.

We have recently reported the possibility to achieve tri- and tetra-nitro-derivatives of corroles, using TFA/NaNO_2 as the nitrating system [12]. In this case, the extreme lability of corrole in acidic media caused both the degradation of the starting material and the concomitant formation of the nitroisocorrole species, which was converted into the aromatic form by metalation with cobalt salt and PPh_3 . Considering the moderate yields of such polynitroderivatives and the presence of a coordinated cobalt ion which cannot be easily removed from the inner core, we decided to attempt polynitration of copper corrolates by using the $\text{AgNO}_2/\text{NaNO}_2$ system, surmising that a suitable increase of silver nitrite would push the nitration beyond disubstitution. In particular we intended to study both the scope of this nitrating system and, eventually, highlight how pyrrolic sub-units react in the case of polysubstitution by means of the isolated products.

We report here the nitration of TiBuPCorrCu performed in DMF using a five molar excess of both AgNO_2 and NaNO_2 . The synthetic routes towards di- and tri-nitrocorrole derivatives discussed in the present work are reported in Scheme 1.

EXPERIMENTAL

General

Silica gel 60 (70–230 mesh, Sigma Aldrich) was used for column chromatography. Reagents and solvents (Aldrich, Merck or Fluka) were of the highest grade available and were used without further purification. ^1H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to residual CHCl_3 (7.25 ppm). UV-vis spectra were measured on a Cary 50 spectrophotometer. Mass spectra (FAB mode) were recorded on a VGQuattro spectrometer in the positive-ion mode using *m*-nitrobenzyl alcohol (Aldrich) as a matrix.

X-ray crystallographic data

Crystals of 3,8,12-(NO_2)₃TtBuPCorrCu for X-ray crystallographic analysis were grown from $\text{CDCl}_3/\text{MeOH}$ solution as the chloroform solvate. Diffraction data for **5** were collected from a very small needle at low temperature on a Bruker Kappa APEX-II Duo diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and an Oxford Cryosystems Cryostream chiller. Refinement was by full-matrix least squares using SHELXL [13], with H atoms in idealized positions, guided by difference maps. The chloroform solvent was disordered, and its electron density was removed using the SQUEEZE [14] procedure. Crystallographic data: $\text{C}_{49}\text{H}_{44}\text{CuN}_7\text{O}_6 \cdot 1.02 \text{ CHCl}_3$, monoclinic space group C2/c , $a = 23.7684(15)$, $b = 27.1189(15)$, $c = 19.3749(19) \text{ \AA}$, $\beta = 124.292(3)^\circ$, $V = 10,317.7(13) \text{ \AA}^3$, $T = 90.0(5) \text{ K}$, $Z = 8$, $\rho_{\text{calcd}} = 1.303 \text{ g cm}^{-3}$, $\mu(\text{CuK}\alpha) = 2.49 \text{ mm}^{-1}$. A total of 14,516 data was collected to $\theta = 55.6^\circ$. $R = 0.090$ for 2458 data with $\text{Fo}^2 > 2$ (Fo^2) of 6151 unique data and 568 refined parameters, CCDC 912670.

Preparation of β -nitrocorrole derivatives

Bis-nitration on TtBuPCorrH₃—TtBuPCorrH₃ (100 mg, 0.14 mmol) was dissolved in DMF (10 mL), and the solution was heated at reflux. Then, NaNO_2 (79 mg, 1.15 mmol) and AgNO_2 (44 mg, 0.28 mmol) were added and the progress of the reaction was followed by TLC analysis and UV-visible spectroscopy. The reaction was complete in 30 min. The reaction mixture was cooled, the product was precipitated by adding distilled water, and then filtered. The crude product was taken-up in CH_2Cl_2 and purified on a silica gel column eluting with CH_2Cl_2 . After the collection of some brownish compounds eluted as a first fraction, the two dinitroisomers corresponding to the 2,3-(NO_2)₂TtBuPCorrH₃ (**1**) (2 mg, 1.8% yield) and the 3,12-(NO_2)₂TtBuPCorrH₃ (**2**) (2 mg, 1.8% yield) were isolated as green fractions. The last fraction was collected and crystallized from $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ giving the 3,17-(NO_2)₂TtBuPCorrH₃ (**3**) as a brilliant green powder (21 mg, 19% yield).

3,17-(NO_2)₂-TtBuPCorrH₃ (3**)**—mp $> 300^\circ\text{C}$. UV-vis (CHCl_3): λ_{max} , nm (log ϵ) 434 (4.51), 484 (4.62), 710 (4.50). ^1H NMR (300 MHz, CDCl_3): δ , ppm 8.81 (s, 2H, -pyrrole), 8.47 (d, 2H, $J = 4.8 \text{ Hz}$, -pyrrole), 8.19 (d, 2H, $J = 4.7 \text{ Hz}$, -pyrrole), 7.96 (m, 6H, phenyls), 7.74 (m, 6H, phenyls), 1.58 (s, 9H, *p*-tBu), 1.54 (s, 18H, *p*-tBu). Anal. calcd. for $\text{C}_{49}\text{H}_{48}\text{N}_6\text{O}_4$: C, 75.0; H, 6.2; N, 10.7%. Found: C, 75.1; H, 6.1; N, 10.6%. MS (FAB): m/z 845 $[\text{M}]^+$.

Synthesis of 3,12-(NO_2)₂-TtBuPCorrCu—Compound (**2**) was dissolved in CHCl_3 and a few drops of a saturated solution of $\text{Cu}(\text{OAc})_2$ in methanol was added. The solution was refluxing for 30 min, then the solvent was evaporated. The crude residue was applied to a silica plug eluting with CH_2Cl_2 to afford the copper complex as an orange fraction. Crystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ afforded the title compound (**4**) in an almost

quantitative yield. The spectroscopic characterization of the product was fully in agreement with data recently reported in the literature [9b].

3,12-(NO₂)₂TtBuPCorrCu (4)—mp > 300 °C UV-vis (CHCl₃): λ_{max} , nm (log ϵ) 466 (4.37), 652 (4.37). ¹H NMR (300 MHz, CDCl₃): δ , ppm 8.36 (s, 1H, β -pyrrole), 7.83 (s, 1H, β -pyrrole) 7.68 (m, 8H, β -pyrroles + phenyls), 7.55 (d, 2H, J = 8.2 Hz, phenyls), 7.44 (m, 6H, phenyls), 1.47 (s, 9H, *p*-tBu), 1.45 (s, 9H, *p*-tBu), 1.42 (s, 9H, *p*-tBu). Anal. calcd. for C₄₉H₄₅CuN₆O₄: C, 69.6; H, 5.4; N, 9.9%. Found C, 69.7; H, 5.2; N, 9.7%. MS (FAB): m/z 845 [M]⁺.

Synthesis of copper(III) β -trinitrocorrolates—To a refluxing solution of TtBuPCorrH₃ (80 mg, 0.11 mmol) in DMF (10 mL) was added Cu(OAc)₂ (23 mg, 0.11 mmol). Completion of the metalation process was monitored by both UV-vis spectroscopy and thin layer chromatography (TLC) analysis. When the copper complex was quantitatively formed, NaNO₂ (40 mg, 0.58 mmol) and AgNO₂ (80 mg, 0.58 mmol) were added and the progress of the reaction was again followed by TLC analysis and UV-vis spectroscopy. After 20 min TLC analysis showed major decomposition of the starting complex together with the formation of a green band. The reaction product was then precipitated by adding distilled water, filtered and washed extensively with water. The crude material was taken-up in CHCl₃ and dried over anhydrous Na₂SO₄. Chromatographic purification of the reaction crude was performed on a silica gel column, eluting with CHCl₃. A first orange fraction was isolated and corresponded to the trinitroisomer 3,8,17-(NO₂)₃-TtBuPCorrCu (**5**) (2 mg, 2%). After collection of traces of 3,17-(NO₂)₂-TtBuPCorrCu, the main green band was isolated and crystallized from CH₂Cl₂/MeOH giving the 2,3,17-(NO₂)₃-TtBuPCorrCu (**6**) as a dark green powder (24 mg, 25% yield).

3,8,17-(NO₂)₃-TtBuPCorrCu (5)—mp > 300 °C. UV-vis (CHCl₃): λ_{max} , nm (log ϵ) 470 (4.35), 582 (4.14), 704 (4.09). ¹H NMR (300 MHz, CDCl₃): δ , ppm 8.35 (s, 1H, β -pyrrole), 8.23 (s, 1H, β -pyrrole), 7.94 (s, 1H, β -pyrrole), 7.68 (m, 7H, β -pyrroles + phenyls), 7.48 (m, 7H, β -pyrroles + phenyls), 1.45 (s, 18H, *p*-tBu), 1.42 (s, 9H, *p*-tBu). Anal. calcd. for C₄₉H₄₄CuN₇O₆: C, 66.09; H, 4.98; N, 11.01%. Found: C, 66.18; H, 5.10; N, 11.14%. MS (FAB): m/z 889 [M]⁺.

2,3,17-(NO₂)₃-TtBuPCorrCu (6)—mp > 300 °C. UV-vis (CHCl₃): λ_{max} , nm (log ϵ) 454 (4.91), 592 (4.51), 729 (4.14). ¹H NMR (300 MHz, CDCl₃): δ , ppm 8.90 (s, 1H, β -pyrrole), 7.62 (m, 7H, β -pyrroles + phenyls), 7.51 (m, 7H, β -pyrroles + phenyls), 1.46 (s, 18H, *p*-tBu), 1.44 (s, 9H, *p*-tBu), 7.43 (br s, 2H, β -pyrroles). Anal. calcd. for C₄₉H₄₄CuN₇O₆: C, 66.09; H, 4.98; N, 11.01%. Found: C, 66.12; H, 5.08; N, 11.10%. MS (FAB): m/z 889 [M]⁺.

RESULTS AND DISCUSSION

The polynitration of metalloporphyrins has been extensively studied and various nitrating systems for pernitration of both *meso*- [15] and β -positions [16] have been reported in the literature. In the latter case for example, the rational use of a HNO₃/CF₃SO₃H/(CF₃SO₂)₂O system generates in high yields a series of β -polynitroporphyrins bearing from one to eight -NO₂ groups, these compounds exhibiting a wide range of redox potentials exploitable in catalysis. On the other hand, the substituted products are obtained as a mixture of isomers, evidencing a poor regioselectivity of the peripheral functionalization.

In this context corroles have demonstrated their originality, giving primarily a single isomer of a β -substituted derivative in spite of their lower symmetry compared with the porphyrin macrocycle. In the case of nitration, the 3-NO₂ isomer was always obtained in different conditions for monosubstitution, as well as the 3,17-(NO₂)₂ derivative for bis-nitration [9,

10, 17]. This selectivity has been also observed in the case of tri-nitration of the gallium complex of F₅TPC, which afforded the 2,3,17-(NO₂)₃ regioisomer as a single reaction product [17]. Relying on the effectiveness of the AgNO₂/NaNO₂ nitrating system shown in our previous work [9b, 9c], we decided to test the generality of this system, investigating the extent to which the nitration on copper corrole could be performed. Undoubtedly polysubstitution by such a system requires increased potential of the oxidant, necessary for the formation of the π -radical cation forms of the nitro-compounds produced as the reaction goes along, which become more resistant to oxidation as the number of NO₂ groups increases. For such a purpose, we performed nitration on TtBuPCorrH₃ similarly to the synthetic protocol recently reported in literature [9b], using both the silver and sodium nitrites in a five-molar excess with respect to the Cu-complex formed *in situ*. The reaction progress was monitored by UV-vis spectroscopy, which showed after 20 min a compound having a broadened Soret band centered at *ca.* 450 nm, along with two satellite bands at about 590 and 720 nm. Chromatographic purification on silica gel using CHCl₃ as eluant firstly afforded traces of an orange fraction, featuring an intense Soret band at 470 nm and two absorptions of lower intensity in the Q-band region at 582 and 704 nm. Even with the small amount of product obtained, we were able to completely characterize it by standard spectroscopic methods. The ¹H NMR spectrum revealed the presence of three different π -pyrrolic protonic resonances at 8.35, 8.23 and 7.94 ppm, respectively, and the integral calculations were consistent with a copper trinitro-derivative, as was further confirmed by the molecular peak at *m/z* 889 provided by FAB MS analysis. The definitive identification of this compound was however accomplished by X-ray crystallographic analysis carried out on crystals obtained by slow diffusion of methanol into a CDCl₃ solution (Fig. 1), which identified the original corrole derivative 3,8,17-(NO₂)₃-TtBuPCorrCu **5** bearing three nitro groups on three different pyrrolic sub-units. The substitution on carbon C8 of the corrole macrocycle was not unprecedented, since we have recently reported it in the case of partial bromination of a Ge complex with a large excess of Br₂. In that case the reaction afforded the hexabromo-derivative with two Br atoms on carbons C8 and C12, confirming these pyrrolic positions as the more reactive compared with the C7 and C13 sites [18].

The Cu atom has square-planar coordination geometry with a slight tetrahedral distortion, with N atoms alternating above and below their best plane by deviations in the range 0.141(6)–0.163(6) Å. The Cu atom lies 0.033(1) Å out of this plane and has Cu–N distances in the range 1.886(6)–1.903(6) Å. The 23-atom corrole core has a slight saddle conformation, with π carbon atoms lying an average of 0.314 Å (range 0.147(10)–0.454(10) Å) out of the corrole best plane. The nitro groups are rotated out of the planes of their respective pyrroles by similar amounts, their planes forming dihedral angles with the corresponding pyrrole planes of 37.5(3)° at C3, 43.2(3)° at C8, and 45.8(3)° at C17.

After traces of copper 3,17-(NO₂)₂ corrole derivative, the column chromatographic purification afforded the main reaction product **6** as a dark green fraction, which was obtained in 25% yield, and showed optical features closely reminiscent of the 3,17-dinitroderivative.

Our attempts to pernitrate the copper corrole to the π -tetranitro level using this oxidizing system were unsuccessful, since the reaction afforded similar results, even with an 8-fold excess of AgNO₂ reagent. It is also worth mentioning that the reaction is sensitive to the nature of the solvent, since in pyridine only bis-nitration is achieved using five-, eight- or fifty-fold [9b] excess of the silver salt.

In light of these recent results, we have analysed all the nitration products obtained both on copper corrolates [9b] and corrole free base [9c] for mono-, bis- and tri-substitution by using appropriate amounts of the AgNO₂/NaNO₂ system. In both cases reactions demonstrated to

be highly selective, affording the 3-(NO₂) and the 3,17-(NO₂)₂ derivatives as the main products for mono- and bis-nitration, respectively. While traces of the monosubstituted isomers 2-(NO₂)TTCorrH₃ and 2-(NO₂) TtBuPCorrCu were also detected, the dinitro-derivatives were differently -substituted. A small amount of a copper dinitrocorrolate was isolated and tentatively identified as the 2,17(NO₂)₂TtBuPCorrCu isomer, on the basis of its proton NMR spectrum [9b] (Fig. 2). The presence of two -pyrrolic singlets at 8.36 and 7.83 ppm and three different *tert*-butyl proton resonances at 1.47, 1.45 and 1.42 ppm respectively was suggestive of an asymmetric substitution, which was supposed to be occurring on C2 and C17 in accordance with the different reactivity always exhibited by pyrrole A and D subunits in peripheral reactions. Thus, the identification of the sites of substitution in such a compound was achieved as a consequence of NMR data and of similar examples in the literature.

The disubstituted isomers of corrole free base were fully characterized as the corresponding Co triphenylphosphine complexes by both traditional spectroscopic techniques and X-ray crystallographic analysis [9c]. In this case the substitution occurred on the same pyrrolic unit, giving the 2,3(NO₂)₂corrole, and quite surprisingly, on the opposite pyrroles A and C, affording the 3,12-dinitroregioisomer. It is worth mentioning that this compound represents the first example in which disubstitution does not involve the usual A and D pyrrolic rings. Tri-nitration gave mainly the 2,3,17-(NO₂)₃ complex and traces of the 3,8,17(NO₂)₃-isomer, the latter showing again the unusual reactivity of pyrrole subunit B toward the nitrating system used.

All those considerations led us to revisit our previous assertion of the 2,17-(NO₂)₂TtBuPCorrCu as the minor product of bis-nitration on copper corrole, and prompted us to find an alternative synthetic route to this compound allowing for its precise identification. For such a purpose, we performed nitration on TtBuPCorrH₃ using a corrole/AgNO₂ molar ratio of 1:2, obtaining the 3,17-(NO₂)₂TtBuPCorrH₃ (**3**) in 19% yield together with small amounts of the 2,3- and 3,12-(NO₂)₂ corroles **1** and **2**, similarly to the reported reaction on TTCorrH₃. The last compound was then metalated with Cu(OAc)₂ and the complex **4** obtained was subjected to spectroscopic characterization. Analyses performed by both UV-vis and ¹H NMR spectroscopic methods afforded spectra completely in agreement with those reported for the putative copper 2,17-(NO₂)₂ corrolate (Figs 2 and 3), indicating C3 and C12 as the correct sites of substitution instead of C2 and C17.

It is worth discussing the electronic spectral features of the prepared copper nitro-derivatives, which showed to be clearly dependent upon which pyrrolic subunit is subjected to substitution. In recent work reporting -nitrotritolyllcorroles, a combination of theoretical studies using DFT and TDDFT methods with crystallographic data revealed the influence of the inserted nitro groups upon the structural, as well as opto-electronic properties of the corrole macrocycle. In particular, these studies showed that the conjugation of the NO₂ group with the -aromatic system of corrole deeply affects some properties of the nitro-derivative, the effect being more pronounced when the insertion occurs at carbon C2 and the substituent is coplanar with the corrole ring.

Considering all the prepared copper nitro-derivatives, we notice that the UV-vis spectral features of the isomers bearing the same number of nitro groups are remarkably different (Fig. 3). In the case of mononitro-derivatives, the 2-NO₂ isomer displays a Soret band centered at 442 nm, red-shifted by *ca.* 7 nm with respect to the 3-substituted analog and the Q-bands region is almost featureless; these variations can probably be ascribable to a strong interaction of the nitro group on C2 with the -system as observed for the same 2-isomer of corrole free base. The difference is more evident for the copper dinitro-derivatives, wherein the B band of the copper 3,8-(NO₂)₂corrole is strongly red-shifted by about 17 nm compared

to the 3,17-isomer. Moreover, their optical spectra are completely different in shape, indicating different electronic transitions occurring in these compounds. The introduction of the third nitro group upon the corrole periphery causes a further red-shift of the Soret band, being located at *ca.* 454 and 470 nm for the 2,3,17- and 3,8,17- trinitro compounds, respectively. The more significant differences involve corroles **4** and **5**, and they can probably be ascribable to the functionalization on the pyrrolenine ring B.

CONCLUSION

In this work we have demonstrated the feasibility of the nitrating system, constituted by silver and sodium nitrites, as a tool for the selective synthesis of copper -trinitrocorrole derivatives, one of which represents the first example of a trisubstituted corrole functionalized on three different pyrrolic units. The unexpected reactivity of pyrrole B under these experimental conditions has prompted us to reconsider our previous results obtained for bis-nitration.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Scheme 1.

Preparation of nitrocorrole derivatives reported in this work. (i) corrole/ $\text{AgNO}_2/\text{NaNO}_2$ (1:2:8), DMF, 30 min; (ii) $\text{Cu}(\text{OAc})_2$, then Cu-corrole/ $\text{AgNO}_2/\text{NaNO}_2$ (1:2:8), DMF, 20 min [9b]; (iii) $\text{Cu}(\text{OAc})_2$, $\text{CHCl}_3\text{-MeOH}$, 30 min; (iv) $\text{Cu}(\text{OAc})_2$, then Cu-corrole/ $\text{AgNO}_2/\text{NaNO}_2$ (1:5:5), DMF, 20 min

Fig. 1.
Molecular structure of **5**, with 50% ellipsoids

Fig. 2.
 ^1H NMR spectrum of 2,17-(NO₂)₂TtBuPCorrCu in CDCl₃

Fig. 3.

(a) UV-visible spectra of 3,12-(NO₂)₂TtBuTPCorrCu (full line) and 3,17-(NO₂)₂TtBuTPCorrCu (dashed line). (b) UV-visible spectra of 3,8,17-(NO₂)₃TtBuTPCorrCu (full line) and 2,3,17-(NO₂)₂₃TtBuTPCorrCu (dashed line)